

***Ab initio* computation of the broadening of water rotational lines by molecular hydrogen**

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Abstract

Theoretical cross sections for the pressure broadening by hydrogen of rotational transitions of water are compared to the latest available measurements in the temperature range 65–220 K. A high accuracy interaction potential is employed in a full close coupling calculation. A good agreement with experiment is observed above ~ 80 K while the sharp drop observed experimentally at lower temperatures is not predicted by our calculations. Possible explanations for this discrepancy include the failure of the impact approximation and the possible role of ortho-to-para conversion of H_2 .

Water is a prominent molecular component of interstellar matter. It has been observed in most astrophysical environments, both in gas and solid phase, as the most abundant poly-atomic molecule [1]. Understanding water spectra is a key to the general thermodynamical budget of astrophysical objects, because of the many allowed spectral transitions, in mm, sub-mm and infra-red regions of the spectrum. Also, the chemical and even exo-biological importance of water cannot be understated. A detailed comprehension of water physical chemistry in various environments is a major goal of the newly launched Herschel Space Observatory (HSO).

In order to extract information from a molecular rotational spectrum, it is essential to model its excitation scheme. Indeed, at low densities, some lines may appear in absorption, some others in emission and there is no *a priori* reason for the molecule under scrutiny to be in thermodynamical equilibrium with the main neutral gas, H_2 . Hence retrieving physical information from spectral lines is only possible with a careful modeling of the interaction of the water molecule with its photonic and molecular environments. Obtaining such models has been a continuous effort in three directions: studies of radiative transfer mechanisms, scattering theory, and very importantly, laboratory experiments capable of testing various theories and models pertaining to collisions [2]. Many comparisons between experiments and theory are nowadays underway, in order to put the water-hydrogen interaction on a firm ground [3–6].

In this communication, we wish to show the first results of a fully *ab initio* computation of pressure broadening cross sections, $\sigma^{\text{p.b.}}(T)$, based on a high precision potential energy surface (PES) for the water-hydrogen interaction [7, 8](hereafter V08), as compared to the very recent experiments of pressure broadening at low temperatures by Dick et al. [9, 10](hereafter DDP10). To our knowledge, it is the first time that such a full *ab initio* pressure broadening quantum calculation is performed for a non-linear molecule in interaction with another molecule. Other comparisons were very successful for simpler symmetries [11–15].

Water being an asymmetric rotor, the rotational levels are usually denoted as $j_{\kappa_a \kappa_c}$ or (j, τ) where j is the rotational quantum number associated with the angular momentum and (κ_a, κ_c) (projections of j along inertia axis) are pseudoquantum numbers, and $\tau = \kappa_a - \kappa_c$. The rotational constants of H_2O are taken at $A = 27.88063134 \text{ cm}^{-1}$, $B = 14.52176959 \text{ cm}^{-1}$, $C = 9.277708381 \text{ cm}^{-1}$. Rotational constant of H_2 is taken at $B = 60.853 \text{ cm}^{-1}$.

Following the experiments of DDP10, we compute here the pressure broadening of the

two spectral transitions connecting the ground states of water: the para 1113 GHz line ($1_{11} \leftarrow 0_{00}$) and the ortho 556 GHz line ($1_{10} \leftarrow 1_{01}$). All our calculations are based on the V08 water-hydrogen full-dimensional PES which was obtained by combining standard CCSD(T) calculations with elaborate explicitly correlated CCSD(T)-R12 calculations. As in Dubernet et al. [16], we have employed the rigid-body version of the V08 PES obtained by averaging the full-dimensional PES over the ground vibrational states of the monomers. Full details can be found in [8].

The broadening of a rotational spectral line because of collision with a buffer gas has been studied theoretically and experimentally for a long time and theory is by now well established. The very general impact approximation states that collision times are much shorter than time between collisions. Within that approximation, which we discuss later, it has been shown that the pressure broadening cross section for the transition from initial state i to final state f , at temperature T , $\sigma_{f \leftarrow i}^{\text{p.b.}}(T)$, may be expressed by closed expressions based on the transition matrix \mathbf{T} [17, 18].

For a broadening coefficient $\Gamma_{f \leftarrow i}(T)$, in frequency/pressure units, Baranger [19] defined the pressure broadening cross section at energy E , $\sigma_{f \leftarrow i}^{\text{p.b.}}(E)$ as

$$\Gamma_{f \leftarrow i}(T) = 1/2 \left\langle n v \sigma_{f \leftarrow i}^{\text{p.b.}}(E) \right\rangle_{T \text{ Boltzmann av.}} \quad (1)$$

where i and f are the initial and final states of the transition, n is the density of the observed molecule, and v is the relative velocity of water and hydrogen. E is the collision kinetic energy. Hence it is possible to define a Boltzmann averaged $\sigma_{f \leftarrow i}^{\text{p.b.}}(T)$:

$$\sigma_{f \leftarrow i}^{\text{p.b.}}(T) = \frac{1}{T^2} \int \sigma_{f \leftarrow i}^{\text{p.b.}}(E) e^{-E/T} E \, dE. \quad (2)$$

Two equivalent ways have been proposed to calculate $\sigma_{f \leftarrow i}^{\text{p.b.}}(E)$, and consequently the averaged $\sigma_{f \leftarrow i}^{\text{p.b.}}(T)$. Following Baranger [17], Schaefer & Monchik [20, 21] and Green [22], we have, for a rotational transition of H_2O ($j_f, \tau_f \leftarrow j_i, \tau_i$), assuming that H_2 remains in an unchanged j_2 state:

$$\begin{aligned} \sigma^{\text{p.b.}}(j_f \tau_f j_2 \leftarrow j_i \tau_i j_2; E) &= \frac{\pi}{k^2} \frac{1}{2j_2 + 1} \sum_{J_i J_f} \sum_{l, l', j_{12} j'_{12}, \bar{j}_{12} \bar{j}'_{12}} X(J_i, J_f, j_i, j_f, l, l', j_{12} j'_{12}, \bar{j}_{12} \bar{j}'_{12}) \quad (3) \\ &\times \left\langle j_2 l_0 j_{12} j_i \tau_i \left| \mathbf{T}^{J_i}(E_i) \right| j_2 l'_0 j'_{12} j_i \tau_i \right\rangle \left\langle j_2 l_0 \bar{j}_{12} j_f \tau_f \left| \mathbf{T}^{J_f}(E_f) \right| j_2 l'_0 \bar{j}'_{12} j_f \tau_f \right\rangle^* \end{aligned}$$

In Eq.(3), j_{12}, j'_{12} are the angular quantum numbers resulting from the coupling of angular momenta j_2 and j_i / j_f (for example, $|j_2 - j_i| \leq j_{12}, j'_{12} \leq (j_2 + j_i)$). l_0, l'_0 are the orbital quantum numbers. $\mathbf{T}^J(E) = 1 - \mathbf{S}^J(E)$ is the transition matrix, at total angular momentum J . The $X(.)$ function groups all angular coupling coefficients and parity sign terms; it is explicit in [21]. E_i and E_f are the two initial and final *total* energies ($E_i \neq E_f$), corresponding to the same kinetic energy, $(\hbar k)^2/2\mu$, μ being the collision reduced mass and k the momentum. A similar equation relevant for H₂O- H₂ coupling may be found in Monchik [21], Eq. (1). It should be noted the $1/(2j_2 + 1)$ factor in front of Eq.(3), lacking in [22] is necessary, as underlined for example in [23].

Baranger, followed by many authors, proceeded to compute the $\sigma^{\text{p.b.}}(E)$ in a different, yet equivalent way, with help of the optical theorem. We have, with nearly the same notations as [17]:

$$\sigma_{f \leftarrow i}^{\text{p.b.}}(E) = \frac{1}{2} \left[\sum_{f'} \sigma_{f' \leftarrow i}^{\text{inel.}}(E) + \sum_{i'} \sigma_{f \leftarrow i'}^{\text{inel.}}(E) \right] + \int |f_i(\Omega; E) - f_f(\Omega; E)|^2 d\Omega \quad (4)$$

In Eq.(4), $\sigma^{\text{inel.}}(E)$ are ordinary *inelastic* cross-sections, i' and f' being all levels connected to f or i at kinetic energy E . The $f_i(\Omega; E)$, $f_f(\Omega; E)$ are the differential *elastic* scattering amplitudes, for the initial and final states, which must be set to interfere before taking the modulus and integrating over all scattering angles Ω .

It must be strongly underlined that both approaches are equivalent. Quite often, since inelastic cross sections or rate coefficients are made available in the literature, in order to have an estimate of $\sigma_{f \leftarrow i}^{\text{p.b.}}(E)$, equation (4) is truncated: only the first two terms, the inelastic cross sections, are used, yielding sometimes to reliable results [24] and sometimes not [13], depending on the structure of the scattering amplitudes (see below).

In order to calculate the \mathbf{T} matrix elements of Eq. (3), we performed a full quantum close coupling scattering computation with help of the Molscat program [25]. The \mathbf{T} matrix elements were subsequently summed at each kinetic energy to get the relevant $\sigma(E)$ cross-sections, inelastic and pressure-broadening. We separately computed collisions of the four symmetry types: (para/ortho H₂O)–(para/ortho H₂). Parameters of the Molscat calculations are similar to the ones used previously[6, 16, 26–28], with the following rotational basis sets: para-H₂: $j_2 = 0, 2$; ortho-H₂: $j_2 = 1$. Ortho and para H₂O: $j_1 \leq 5, 6, 7$, for

increasing collision energy. For $E < 20 \text{ cm}^{-1}$, the hybrid modified log-derivative/Airy propagator of Manolopoulos and Alexander was used; above that energy, the diabatic modified log-derivative method of Manolopoulos was used [25]. We checked convergence with respect to basis set size, maximum range of radial integration and size of step in the radial propagation. The collision energy range was $0.5 \leq E \leq 350 \text{ cm}^{-1}$, with increments ΔE small enough to roughly describe resonances. Decrease of the ΔE step did not change significantly the averaged $\sigma_{f \leftarrow i}^{\text{p.b.}}(T)$, which was obtained by a numerical integration of Eq. (2). At collision energies $E > 350 \text{ cm}^{-1}$, $\sigma^{\text{p.b.}}(E)$ remains essentially flat and was therefore extrapolated as a constant.

Results are presented in figures 1 and 2. In addition to the pure ortho H_2 (blue lines) and para H_2 (red lines) cross sections, we added two possibilities for the ortho-to-para ratio (OPR) of H_2 : the solid black lines suppose a “normal” OPR value of 3, as expected in the DDP10 experiment. The grey solid lines suppose that the thermodynamical equilibrium OPR value is reached at each temperature T , as if ortho to para transitions were possible. In both figures, the results of DDP10 are shown as green open symbols, with their exact values provided courtesy of B. Drouin.

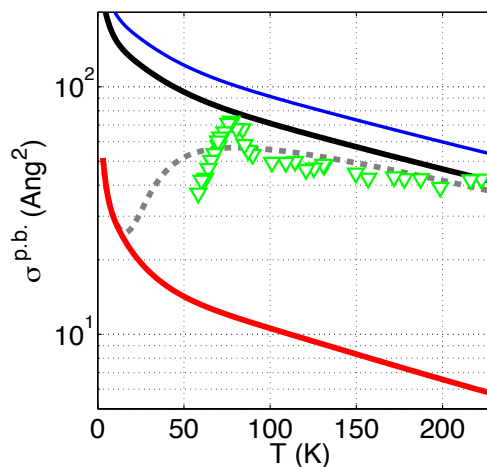


FIG. 1: Pressure broadening cross-sections for the transition at 556 GHz, ortho- H_2O , $1_{10} \leftarrow 1_{01}$. Theory: Red line, below, pure para- H_2 collisions; blue line above, pure ortho- H_2 collisions. Black continuous line, OPR value, 3; grey dashed line OPR value at equilibrium for each T . Green triangles, experimental values taken from [10].

Several points may be seen by inspection of figures 1 and 2. If we assume an OPR value of

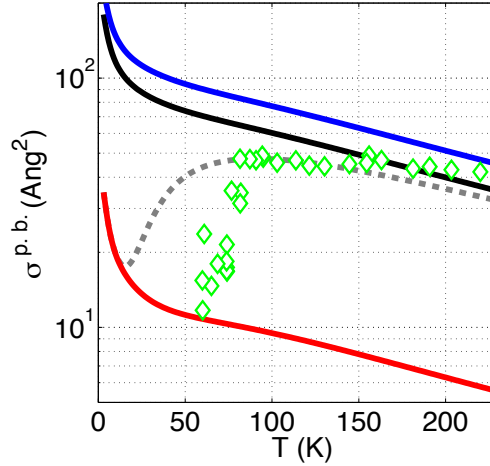


FIG. 2: Pressure broadening cross sections for the transition at 1113 GHz, para-H₂O, $1_{11} \leftarrow 0_{00}$. Same caption as for figure 1.

3, we see that the theory vs. experiment agreement is very good (within 30%) for $T \gtrsim 80$ K. Let us recall that there are no adjustable parameters involved in the simulation, except for the OPR value. This agreement should come at no surprise, since recent analogous calculations on branches of Raman spectra show similar successes [11, 23, 29, 30]. Both these calculations and ours make use of state-of-the-art *ab initio* PES as well as fully converged close-coupling calculations. Within the impact approximation valid at these temperatures and moderate densities ($n \lesssim 1$ amagat), Baranger formalism [17], equation (3), is essentially exact for nonoverlapping lines. The whole uncertainty that arises is due either to inadequacies of the impact approximation, which is to be ruled out here at $T > 80$ K (see for example [18] or [31] for a discussion) or else to imprecision of the PES. We see thus that we actually test the PES by comparing experimental pressure broadening with careful quantum calculations, in the relevant density and temperature ranges.

Pressure broadening cross sections, at these intermediate temperatures, are sensitive to the overall shape of the PES, and especially to the isotropic part. This may be understood in two ways. First, the \mathbf{T} matrix elements actually used in Eq.(3) are elastic in the rotational quantum numbers, thus non-zero also for an isotropic potential energy surface. Second, this is confirmed by the good quality of pressure broadening coefficients obtained by approximate semi-classical methods, where the impinging trajectory of the perturber is totally decoupled from the tensorial nature of the molecule/molecule electromagnetic interaction [31–33]. In

retrospect, we understand that approximating the full Eq.(3) by the purely inelastic terms of Eq.(4) may be correct in certain cases, but this should at least be carefully checked. An analogous point has been made earlier, see [23].

We show in figure 3 the present results as compared to estimates based on the inelastic sum, Eq. (4), but truncated to the first two terms, as used by DDP10 (and corrected for an error of a factor of 2 for the Dubernet et al. data). We see that there is a strong disagreement between the two computational schemes. In particular, data computed from the inelastic rates of Dubernet et al. [16], which are based on the same PES as the present work, are significantly lower than the present rigorous calculations. The observed differences are to be attributed to the approximation in applying the Random Phase Approximation (neglect of the elastic scattering interference term) to Eq. (4). Furthermore, DDP10 made the further simplification of replacing the averaging procedure of Eq. 2 by using rate coefficients divided by the average thermal velocity. While this should not change the trend of the $\sigma^{\text{p.b.}}(T)$, it adds some further imprecision. For $T > 20$ K, the DDP10 points were extracted, via the same procedure, from the older values of Phillips et al. [34] based on a less accurate PES. We note that the same procedure was also applied by DDP10 to the case of $\text{H}_2\text{O}-\text{He}$ where it was found to be quite accurate, suggesting a very different structure of the scattering amplitudes. This is actually not surprising since *i)* the $\text{H}_2\text{O}-\text{He}$ and $\text{H}_2\text{O}-\text{H}_2$ PES are very different (see, e.g., [3, 4]) and *ii)* additional coupling terms are introduced by the rotational angular momentum of H_2 .

The low temperature range of the theory vs. experiment comparison, $T \lesssim 80$ K, is more problematic. Experiments show a dramatic *decrease* of $\sigma^{\text{p.b.}}(T)$ as T goes below about 80 K, for both transitions examined here and also for higher transitions. An analogous, even if less pronounced effect was also found for $\sigma^{\text{p.b.}}(T)$ in [12, 13], for $\text{HCN}-\text{He}$ and $^{13}\text{CO}-\text{He}$ respectively, albeit at much lower T , around 5K. No definite explanation may be found in these preliminary calculations, but it must be noted that disagreement between computations and experiments arise at energies where the pressure broadening and inelastic cross sections enter in a regime where narrow resonances become prominent, see e.g.[28]. If resonances are sufficiently narrow, that is, if the complex $\text{H}_2\text{O} - \text{H}_2$ is sufficiently long-lived, the impact approximation may be no longer valid. According to the density in the DDP010 experiment ($n \sim 10^{20} \text{ cm}^{-3}$, B. Drouin, private communication), and with a cross-section of about $\sigma^{\text{p.b.}}(E = 80 \text{ K}) \simeq 50 \text{ \AA}^2$, an average speed of $v = \sqrt{2E/\mu} \simeq 1 \text{ km/sec}$, and a

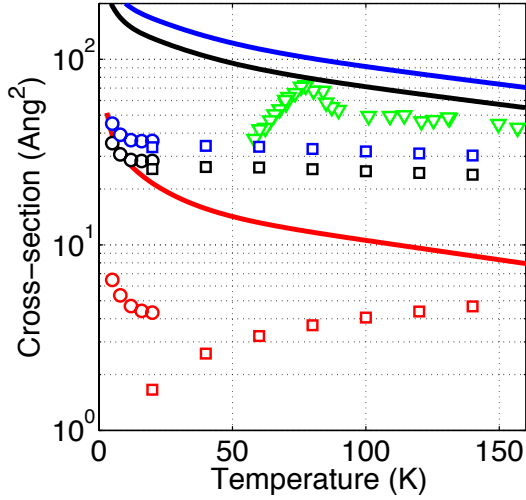


FIG. 3: Pressure broadening cross-sections for the transition at 556 GHz, ortho-H₂O, $1_{10} \leftarrow 1_{01}$. Blue, red and black continuous lines, present theories, as in figure 1. Open symbols, summation of inelastic scattering cross sections as in DDP10, circles from Dubernet et al., 2002, squares, from Green et al., 1996, with color scheme identical to the solid lines. Green triangles, experimental values taken from DDP10.

resonance width of about $\Gamma \simeq 1 \text{ cm}^{-1}$ [16], we have that the interaction volume U becomes comparable to the inverse density [19] :

$$U = (h\nu\sigma^{\text{p.b.}}/\Gamma) \simeq 1.6 \cdot 10^{-20} \text{ cm}^3 \sim 1/n \simeq 10^{-20} \text{ cm}^3, \quad (5)$$

invalidating the impact approximation. It is also possible that, for yet unknown reasons, there is a dramatic conversion from ortho-H₂ to para-H₂ at low temperatures, through some paramagnetic impurities in the walls of the cell [35], even if there is no experimental hint that indicates this explanation at the moment. Further insight is obviously needed in those regimes. Measurements with para-H₂($j = 0$) would be particularly valuable both for comparison with theory and for applications to cold interstellar clouds where H₂ is mostly in its para form [36].

In this Communication, we have shown using full quantum scattering methods combined with state-of-art PES, that very good agreement is found between experimental pressure broadening and theoretical calculations at temperatures where the impact approximation is clearly valid, i.e. $T \gtrsim 80 \text{ K}$. We have found that the rigorous theory of Baranger is needed to make valuable predictions for the present system and that simple approximations based on the manipulation of inelastic rates or cross sections are unreliable. We stress in

particular that the sharp drop observed in the pressure broadening measurements below ~ 80 K, and not predicted by the present calculations, does not cast doubt on the inelastic rates computed by Dubernet et al. [6, 16, 26] since a rigorous quantum theory of broadening beyond the impact approximation seems necessary in this regime, as discussed above. As a result, to our opinion, the water-hydrogen V08 PES is once more successfully tested, with a special emphasis on the mid- to long-range region of the PES and the isotropic part. We thus complement here various tests performed recently on the water-hydrogen system, such as differential measurements [4], and molecular beam scattering experiments [5], which have all so far confirmed the high accuracy of the V08 PES. Another series of experiments, now underway, would aim at the spectroscopy of the bound $\text{H}_2\text{O}-\text{H}_2$ van der Waals molecule. With all these tests completed in the near future, the V08 PES will be thoroughly tested and extremely good confidence should be gained for all astrophysical applications.

Acknowledgments

We thank B. Drouin for communicating detailed experimental data as well as F. Thibault for useful insights. This project is partly supported by the Institut National des Sciences de l'Univers through its program Physico-Chimie de la Matière Interstellaire and by the CNES. The Laboratoire d'Astrophysique is a joint CNRS/Université Joseph-Fourier institute, under the name UMR 5585.

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